# Physical Properties of Alum-Retanned Vegetable Leathers*

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The authors[1] have shown previously that alum retannage gives vegetable leathers a high degree of resistance to acid deterioration. The results indicated the desirability of further study of this type of leather to determine other properties that may have a bearing on commercial applications.

For this study six sets of leathers were tanned in the laboratory—two of steer hide, two of calfskins, one of sheepskin, and one of cow grain split. Each set consisted of three or four pieces about 8 by 12 inches, taken from directly comparable positions in the same hide or skin. The sheepskin was tanned with sulfited quebracho; a blend of chestnut and sulfited quebracho was used for the rest of the leathers. One piece of each set was retanned with alum and one with chrome for comparison. The remaining pieces were used without further treatment as controls. The methods of retannage were the same as those used in previous studies[1]. For the alum retannage an aluminum sulfate solution was used which was one-quarter neutralized with sodium carbonate and contained sodium chloride equal in amount to the aluminum sulfate. For the chrome retannage a chrome alum solution one-third neutralized with sodium carbonate was used. Significant analytical data on these leathers, obtained by the Official methods of the A.L.C.A., are presented in Table I.

The leathers were subjected to a series of physical tests. Tensile strength, percentage of stretch, and resistance to tear were determined by a Schopper or Scott testing machine of suitable capacity; resistance to bursting was determined by a Jumbo Mullen tester; resistance to folding was determined by the apparatus devised by Clarke and Frey[2]; porosity to air, permeability to water vapor, and water absorption were determined essentially by the methods described by Wilson and Merrill[3]. The shrinkage temperature was determined on a strip of leather about one-eighth of an inch wide and one and one-half inches long. This was fastened at each end along the bulb end of a thermometer. The strip was not drawn tightly against the side of the thermometer but was curved out in the form of a bow extending about one-quarter of an inch at the point of widest separation. The thermometer with leather attached was immersed in glycerin, which was then slowly heated. As the shrinkage temperature was reached there was a sudden contraction in volume of the leather strip, which could easily be noted by observing the flattening of the leather against the side of the thermometer. A qualitative test of the

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TABLE I. ANALYSIS OF LEATHERS (*moisture-free basis*)

| Kind of Skin or Hide | Tannage | Total Ash Per cent | $Al_2O_3$ or $Cr_2O_3$ Per cent | Soluble Non-Tannin Per cent | Soluble Tannin Per cent | pH | Combined Tannin Per cent | Degree of Tannage |
|---|---|---|---|---|---|---|---|---|
| Steer hide I | | | | | | | | |
| | Vegetable control | 0.3 | .. | 2.8 | 13.8 | 3.5 | 26.3 | 53 |
| | Vegetable and alum retan | 2.3 | 2.1 | 1.7 | 5.7 | 3.5 | 32.5 | 63 |
| | Vegetable and chrome retan | 2.4 | 2.0 | 1.4 | 3.1 | 3.2 | 35.9 | 72 |
| Steer hide II | | | | | | | | |
| | Vegetable control | 0.6 | .. | 4.1 | 12.2 | 3.8 | 35.2 | 76 |
| | Vegetable and alum retan | 3.3 | 2.8 | 3.2 | 7.5 | 3.3 | 39.9 | 90 |
| | Vegetable and chrome retan | 3.3 | 2.9 | 2.8 | 5.2 | 3.2 | 42.3 | 98 |
| Calfskin I | | | | | | | | |
| | Vegetable control | 0.3 | .. | 2.0 | 6.7 | 4.0 | 28.9 | 48 |
| | Vegetable and alum retan | 2.3 | 2.1 | 1.9 | 3.0 | 3.6 | 31.1 | 53 |
| | Vegetable and chrome retan | 2.7 | 2.1 | 1.5 | 1.7 | 3.3 | 35.4 | 62 |
| Calfskin II | | | | | | | | |
| | Vegetable control | 0.5 | .. | 1.3 | 2.1 | 3.6 | 37.3 | 72 |
| | Vegetable and alum retan | 4.8 | 3.7 | 0.6 | 0.7 | 4.1 | 41.6 | 86 |
| | Vegetable and chrome retan | 3.9 | 3.4 | 0.9 | 0.9 | 3.5 | 40.9 | 86 |
| Sheepskin | | | | | | | | |
| | Vegetable control | 1.4 | .. | 2.4 | 4.1 | 4.2 | 33.3 | 64 |
| | Vegetable and alum retan | 4.7 | 3.5 | 0.3 | 0.3 | 4.5 | 43.1 | 90 |
| | Vegetable and chrome retan | 4.3 | 3.7 | 0.2 | 0.1 | 4.1 | 40.7 | 83 |
| Cow grain split | | | | | | | | |
| | Vegetable control | 0.5 | .. | 2.4 | 8.1 | 4.0 | 28.6 | 54 |
| | Vegetable and alum retan | 2.3 | 2.2 | 1.5 | 2.8 | 3.8 | 33.2 | 63 |
| | Vegetable and chrome retan | 2.7 | 2.0 | 1.2 | 1.5 | 3.4 | 37.8 | 79 |

resistance to moist heat was made by immersing strips in boiling water for three minutes. Any change in the condition or area of the strips was noted. The results of the physical tests are given in Table II.

Table II shows that within the limits of experimental error neither alum nor chrome retannage has caused any appreciable change in the strength of the vegetable leathers, whether measured as tensile strength or resistance to tearing, bursting or folding. The stretch of the leathers is also unaffected, although straight chrome or alum leather has a natural stretch greater than that of straight vegetable leather. The figures for porosity, permeability and water absorption indicate that retannage has improved the ventilating properties of the vegetable leathers. The resistance to wetting and to water

TABLE II. PHYSICAL PROPERTIES OF VEGETABLE ALUM-RETANNED AND CHROME-RETANNED LEATHERS

| Kind of Skin or Hide | Tannage | $Al_2O_3$ or $Cr_2O_3$* | Thickness | Tensile Strength | Stretch at Breaking Point | Tear Strength | Bursting Strength | Folding Strength† | Porosity‡ | Relative Permeability to Water Vapor | Water Absorption§ First Period | Water Absorption§ Second Period | Shrinkage Temperature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Per cent | Inches | Lbs./sq.in. | Per cent | Lbs. | Lbs. | No. of Folds | mls./min./sq. cm. | | Per cent | Per cent | Degrees C. |
| Steer hide I | Vegetable control of alum retannage | .. | 0.249 | 2,900 | 29 | .. | .. | .. | 176 | 0.60 | 33.1 | 45.0 | 80 |
| | Alum retannage | 2.1 | 0.222 | 2,860 | 30 | .. | .. | .. | 146 | 0.64 | 25.6 | 38.0 | 105 |
| | Vegetable control for chrome retannage | .. | 0.222 | 3,360 | 32 | .. | .. | .. | 176 | 0.60 | 33.1 | 45.0 | 80 |
| | Chrome retannage | 2.0 | 0.228 | 3,170 | 36 | .. | .. | .. | 167 | 0.66 | 27.1 | 39.9 | 105 |
| Steer hide II | Vegetable control for alum and chrome retannage | .. | 0.234 | 1,900 | 22 | .. | .. | .. | 151 | 0.49 | 47.4 | 51.8 | 87 |
| | Alum retannage | 2.8 | 0.245 | 2,020 | 30 | .. | .. | .. | 334 | 0.64 | 32.5 | 43.7 | 112 |
| | Chrome retannage | 2.9 | 0.240 | 2,291 | 31 | .. | .. | .. | 196 | 0.54 | 36.5 | 44.9 | 110 |
| Calf-skin I | Vegetable control for alum retannage | .. | 0.090 | 3,470 | 38 | .. | .. | .. | 180 | 0.77 | 58.5 | 67.3 | 83 |
| | Alum retannage | 2.0 | 0.090 | 3,060 | 30 | .. | .. | .. | 242 | 0.78 | 14.7 | 53.4 | 102 |
| | Vegetable control for chrome retannage | .. | 0.125 | 3,450 | 30 | .. | .. | .. | 180 | 0.77 | 58.5 | 67.3 | 83 |
| | Chrome retannage | 2.0 | 0.127 | 3,110 | 29 | .. | .. | .. | 270 | 0.74 | 17.5 | 54.9 | 104 |
| Calf-skin II | Vegetable control for alum and chrome retannage | .. | 0.039 | 5,540 | 38 | 27.5 | 1,195 | 373 | 129 | 0.70 | 61.7 | 68.2 | 70 |
| | Alum retannage | 3.7 | 0.044 | 5,370 | 33 | 27.1 | 1,188 | 498 | 185 | 0.69 | 11.2 | 51.9 | 112 |
| | Chrome retannage | 3.4 | 0.036 | 5,210 | 32 | 26.6 | 1,245 | 494 | 192 | 0.81 | 16.8 | 59.0 | 107 |
| Sheep-skin | Vegetable control for alum and chrome retannage | .. | 0.050 | 1,810 | 33 | 11.9 | 532 | 221 | 218 | 0.86 | 191.5 | 209.7 | 72 |
| | Alum retannage | 3.5 | 0.043 | 1,760 | 29 | 11.4 | 504 | 275 | 436 | 0.89 | 22.4 | 80.1 | 113 |
| | Chrome retannage | 3.7 | 0.036 | 1,790 | 31 | 11.7 | 491 | 235 | 308 | 0.89 | 21.9 | 74.8 | 110 |
| Cow grain split | Vegetable control for alum retannage | .. | 0.062 | 1,790 | 53 | 18.4 | 727 | 330 | 595 | 0.84 | 82.1 | 95.1 | 87 |
| | Alum retannage | 2.1 | 0.068 | 1,830 | 38 | 18.7 | 694 | 374 | 720 | 0.86 | 18.9 | 47.2 | 111 |
| | Vegetable control for chrome retannage | .. | 0.055 | 1,590 | 46 | 18.4 | 727 | 330 | 595 | 0.84 | 82.1 | 95.1 | 87 |
| | Chrome retannage | 2.0 | 0.066 | 1,240 | 46 | 18.6 | 703 | 342 | 702 | 0.83 | 20.2 | 52.3 | 110 |

*Expressed on basis of moisture-free leather.
†Load applied to leathers was 5 kgs. for the calfskin and 2 kgs. for the sheepskin and cow grain split.
‡Vacuum of 63.5 cm. used for all leathers except sheepskin on which it was necessary to reduce vacuum to 5 cm.
§First period was two hours for the steer hide, one-half hour for others; second period was twenty-four hours in every case.

absorption has been increased considerably, while at the same time the resistance to the passage of air through the leathers has, in general, been decreased and the passage of water vapor has been only slightly affected.

The data on shrinkage temperature show an important property of the retanned leathers and suggest that these leathers may be useful for many purposes where they are exposed to heat, particularly moist heat. The shrinkage temperatures of the straight vegetable leathers are all well below the boiling point of water, while those of the retanned leathers are all considerably above this temperature. Furthermore, qualitative examinations of pieces subjected to the boiling test showed that whereas the vegetable leathers were made hard, horny and cracky, and therefore worthless, the retanned leathers were only slightly affected.

In these tests, as in the previous study of the resistance to acid deterioration, alum retannage was found superior to chrome retannage. Other advantages in the use of alum over chrome are lower cost, availability of material, and improved color in the leather produced.

These leathers have been tanned first with a vegetable tannage and retanned with alum or chrome. In the commercial tanning of combination vegetable-chrome leather it is the usual practice to reverse this order, that is, to tan with chrome first and follow with a vegetable retannage. A study was carried on to determine whether a vegetable retannage of alum leather is practical. For these experiments hide powder was used. Twelve lots of powder were tanned with alum, varying the amount of alum used, the pH of the solutions during tanning, the amount of neutralization, and the aging after tanning. After tanning and aging, the leathers were washed with water until the washings showed only negligible amounts of aluminum. This indicated that the $Al_2O_3$ remaining in the leathers, ranging from 0.5 per cent to 4.8 per cent by analysis, was almost irreversibly combined with the hide substance. The leathers were next retanned with a vegetable tanning material. As the tanning progressed, the liquors became contaminated with aluminum salts, and analysis of the leathers showed that the $Al_2O_3$ content decreased in proportion to the amount of tannin combined. The vegetable retannage of alum leather is a process of substitution of vegetable tannin for combined $Al_2O_3$. The analytical figures for the leathers tanned in the reverse order show that the alum does not replace the combined tannin but that the effect of the two tannages is additive. It is possible that under proper conditions vegetable retannage of alum leathers could be conducted without loss of $Al_2O_3$, but under normal tanning conditions it would appear to be more practical to tan in the reverse order.

*Conclusions*

Alum or chrome retannage of vegetable leathers has practically no effect on the stretch of the leathers or on their strength, whether measured as tensile strength or resistance to tearing, bursting, or folding.

Retannage improves the ventilating properties of leathers by increasing their porosity to air and resistance to wetting and water absorption, the permeability to water vapor remaining constant.

The resistance of the retanned leathers to heat is much superior to that of the straight vegetable leathers. The retanned leathers are almost unaffected by immersion in boiling water for three minutes. Their shrinkage temperatures are from 5° to 13° C. above the boiling point of water, whereas those of the straight vegetable leathers are from 13° to 30° below this temperature.

The order of tannage of combination vegetable-alum leather should be vegetable followed by alum, as the reverse order leads to the replacement of combined $Al_2O_3$ by tannin.

In all our tests, alum retanned leathers are at least equal, and in most cases superior, to chrome retanned leathers in strength and resistance to heat and acids. They have the further advantages of a lighter color and the use of cheaper and more readily available material in their production.

Under present conditions alum retannage should be of particular interest. The probability of increasing difficulty in obtaining chromium salts makes the substitution of cheaper, more easily obtainable aluminum salts very desirable. Furthermore, the increased durability of alum retanned leathers as compared with straight vegetable leathers makes their use advantageous for purposes involving exposure to acids or to high temperatures.

The leathers considered in this study have all been tanned in the laboratory. The question arises whether commercial tanning would produce leathers of as good quality and whether difficulties would arise in the tanning process. In a later paper we shall give results obtained by gas chamber exposure tests of commercial retanned alum leathers that partly answer this question. Results of exposure tests on some of the leathers used in this study will also be given.

## References


1. The Permanence to Acid Deterioration of Vegetable Leathers Retanned with Alum. *J.A.L.C.A.*, 35, 440 (1940).
2. Some Results with a New Folding Endurance Tester for Light Leather. *J.A.L.C.A.*, 28, 77 (1933).
3. Analysis of Leather. Wilson and Merrill, pp. 102-111 (1931).


## *Discussion*

F. E. Smith: These tests made by Dr. Frey have been very interesting, and seem to indicate a great increase in the use of alum when compared with chrome; and we have been told before that chrome has given, especially in lighter leathers, a greater permeability and resistance to wear. As I recall, a statement was made of a definite solution of alum that was made. I was wondering whether the effect of percentage range of alum would have any indication of greater or lesser effect, particularly in the boiling range, and for deterioration. I would like to ask whether the method of fat-liquoring would have any effect on the tensile strength and the stretch in any way, more so than on the straight vegetable tan alone.

J. S. ROGERS: A study has been made of the effect of variations in the alum content of similar leathers. The results of deterioration tests for leathers of approximately 1.5 and 3 per cent $Al_2O_3$ have already been published. It was shown that 1.5 per cent $Al_2O_3$ imparts marked protection to straight vegetable tanned leather and that this is further increased at a content of 3 per cent $Al_2O_3$. Physical properties such as shrinkage temperature vary in a similar manner.

Fat-liquoring would have a marked influence on the quality of the leathers. To determine the proper fat liquor would require considerable study not directly pertinent to the present experiments and would also introduce into the tannage a further factor difficult to control. It was, therefore, decided to reduce the effect of the oil to negligible proportions by using on the leathers only minimum amounts of oil. This was done only for the purpose of ease of comparison in our tests and it is to be expected that in practice a suitable fat-liquor would be used.

A. N. KAY: Did I understand you to say that the retanning solution was plus an equal amount of sodium chloride? Also, how was the color of the vegetable tanned leather affected? And, lastly, how was the analysis of the leather affected, especially the pH?

ROGERS: I think the figures are all shown in the tables. The vegetable leather that was retanned by alum was lighter in color.

A. H. WINHEIM: I would like to ask three questions. In the first place, in your Table No. I, were those aluminum oxide and chromium oxide figures calculated to a moisture and fat-free basis, or to a hide substance basis?

H. B. WALKER: I think the footnote on the slide said moisture-free basis.

WINHEIM: Another point you may have touched upon and I may have missed, was regarding the nature of vegetable tannage. Do you know the approximate time consumed, and whether or not it was run in a drum or vat?

ROGERS: The nature of the tannage was a 50-50 blend of sulfited quebracho and chestnut except in the case of the sheepskin leather which was tanned in quebracho only. The thinner skins were tanned in a small laboratory drum for three days. The thicker skins and hide were tanned in our experimental rocker vats, the liquor being strengthened, each day some of the tan liquor being removed and stronger, fresh liquor added. The time of tannage varied from two to six weeks, dependent upon thickness. In every case an attempt was made to produce a degree of tannage corresponding to usual practice for the type of leather desired.

WINHEIM: The other factor has some bearing on availability. Although iron-free aluminum sulfate is rather easy to get, I understand the impure forms are more easily obtained. Do you know the nature of the color effect that might be occasioned by the use of aluminum sulfate containing small traces of iron?

ROGERS: No, I do not know. That would depend on how much iron was present, and if the iron content was appreciably high it would probably give some difficulty.

WALKER: I suppose, Mr. Rogers, that these leathers re-tanned with alum were washed off in being retanned; and that in the finally dried leather the aluminum present was securely fixed so that it would not come off. I am thinking of the possible complication of the precipitating effect of the alum in the leather on some of the finishing compounds that are commonly used today. Some people know—we certainly do—that alum leathers generally are a headache to finish because of the precipitating effect of the alum.

ROGERS: This possible difficulty has occurred to us and is mentioned in the text but in our later work we have some leathers that have been commercially tanned, finished, and dyed. This shows that at least in some types of finishing and dyeing this difficulty has been successfully met.

H. BIRKENSTEIN: What was the comparative weight between the chrome retanned and the alum retanned leather? In other words, the thickness of the leather?

ROGERS: The thickness measurements of the leather are given in the tables. It should be remembered that the different pieces of leather were originally taken from the skins or hides in such a way as to be directly comparable between the three different types of tannage.

R. HORWEEN: Did I understand you to say that the alum solution was prepared by the addition of sodium carbonate?

ROGERS: Yes.

HORWEEN: That raises the question as to whether any investigation was made regarding the possible differences in result with different degrees of acidity of the aluminum sulfate salt.

ROGERS: The question of basicity of the alum solutions was investigated in preliminary tannages. It was found that the most favorable basicity was that produced by adding sodium carbonate to the alum solution almost to the verge of precipitation.

HORWEEN: How much sodium carbonate was used?

ROGERS: If I recall correctly, I think in this case the alum was one-quarter neutralized.

A. SCHUBERT: I believe it probably will be several days, or perhaps weeks, before we begin to appreciate how much this paper really means. This I believe is really one of the most important contributions that has so far been made at this meeting. It is very far-reaching. The fact that the results are what they are means that a leather with great possibilities for use for Army shoe uppers can be made this way.

In making these retan tests was the leather crusted or dried out before the retanning was done, or was it done immediately after the vegetable tanning and before it was dried?

ROGERS: In our preliminary tests it was found that it was immaterial whether the alum retannage was done immediately after vegetable tannage and washing or upon the dried leather. In these tests for ease of calculation the leathers were dried before the alum retannage.

SCHUBERT: In the fat liquors, what type was used?

ROGERS: They were not fat-liquored.

SCHUBERT: You also stated in your talk that the vegetable was substituted by the alum?

ROGERS: Not that way—it was the other way around. If you tan first with alum and then retan with vegetable, there is a tendency for the alum to be taken out and substituted by the vegetable.

SCHUBERT: But not in this case where you finish with the alum?

ROGERS: That is right.

SCHUBERT: When you finished up the leather and made your tests did you wash out all the sodium chloride or did you permit the sodium chloride, present in your alum solution, to remain in the leather and dry with the leather?

ROGERS: The leathers were washed after retannage. The residual sodium chloride is low.

SCHUBERT: A question was asked about the iron present normally in the so-called impure form, or not iron-free alum. This percentage is generally so small (I have had practical experience with it) that it would not materially affect the color.

WINHEIM: The amount is probably reduced by ordinary alkalinization so that it would take care of it?

SCHUBERT: Right.

HORWEEN: It may be interesting to note, sir, that the tannage with alum and then retannage with vegetable materials is pretty old. In our plant, for instance, there was an old process in which that was used; and it is pretty clear that practically all of the alum was replaced with vegetable material. As nearly as I can gather, the purpose of the alum was to set the grain, to keep the grain in a smooth condition and make it possible to speed up the vegetable tanning.

ROGERS: We have done some work along that line, and it has been our experience that there seems to be a difference in the character of the leather produced when we give a preliminary tannage with alum followed by vegetable, although most of the alum did come out. The leather was definitely different than if tanned with a straight vegetable tan. We have been investigating possible procedures for the more permanent fixing of the alum in an alum tannage, to be followed possibly by a vegetable tan. But we are not in a position to make a report on that yet.

O. Reethof: What Dr. Schubert said regarding army retanned is of great interest. The only thing is what the Federal specifications would say about it; because the specifications call for a certain percentage of chrome. So the specifications would have to be changed so that the chrome could be replaced by a certain percentage of alum.

Schubert: It is understood that under the present specifications it could not be done; but there is nothing to prevent the specifications being changed should the necessity arise, and should this leather be proven as good as or better than the present type of retan. During a war a lot of things are possible.

There is an old maxim that in any combination of tannage the first tannage generally carries its character through. So if you have an alum tannage first, no matter how much you retan it, alum characteristics always follow through to the finished leather. This is true of chrome-vegetable or vegetable-chrome, or any other combination. The character of the first tannage is always noticeable in the finished leather.